PCT
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B32B 7/10

A1

(11) International Publication Number: WO 94/08781

(43) International Publication Date: 28 April 1994 (28.04.94)

(21) International Application Number: PCT/US93/09996

(22) International Filing Date: 19 October 1993 (19.10.93)

(30) Priority data:
07/963,674 20 October 1992 (20.10.92) US

(71) Applicant: AVERY DENNISON CORPORATION [US/US]; 150 N. Orange Grove Boulevard, Pasadena, CA 91109 (US).

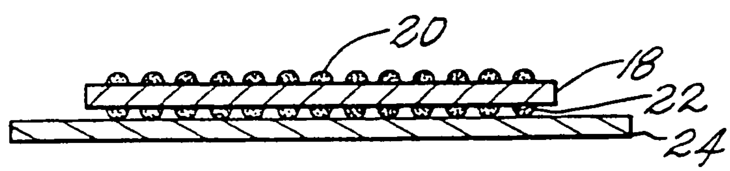
(72) Inventors: VARGAS, Richard, R. ; 11724 Garfield Avenue, Southgate, CA 90280 (US). PLAMTHOTTAM, Sebastian, S. ; 1496 Moonridge Court, Upland, CA 91786 (US). LANDERS, John, O. ; 2610 Bernwood Street, Duarte, CA 91010 (US).

(74) Agent: GRINNELL, John, P.; Christie, Parker & Hale, P.O. Box 7068, Pasadena, CA 91109-7068 (US).

(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: PRESSURE-SENSITIVE STRUCTURAL ADHESIVE



(57) Abstract

A pressure-sensitive structural adhesive is formed by applying a thin layer of pressure-sensitive adhesive (20, 22) to one or both sides of a core layer (18) of partially cured structural adhesive. The pressure-sensitive adhesive provides a tacky surface allowing a temporary bond at room temperature. Upon curing of the construction, the bond properties change to that of a structural adhesive, providing a strong permanent bond. Upon cure, the skin layer or layers of pressure-sensitive adhesive are absorbed into the layer of structural adhesive.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovak Republic
SN	Senegal
TD	Chad
TG	Togo
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

PRESSURE-SENSITIVE STRUCTURAL ADHESIVE

Field of Invention

This invention provides a novel pressure-sensitive structural adhesive construction which is normally tacky and forms a pressure-sensitive adhesive bond at room temperature, which bond on heat activation is supplanted by a structural adhesive bond.

Background of the Invention

Structural adhesives such as cyanoacrylate epoxy resins and the like are well-known for providing strong and permanent bonds. However, before curing, such adhesives do not normally provide aggressive adhesive qualities and, therefore, require external aids such as clamping devices to hold the substrates to be bonded together until cure has been completed and a structural bond formed.

Tacky, pressure-sensitive adhesives have been known for many years and have been used in various bonding and fastening applications. They provide a flexible bond and are used in a wide range of applications including adhering labels, decals, and bonding automotive trim parts and name plates to various substrates. However, they show substantially lower strength characteristics compared to a structural adhesive like cured epoxy or cyanoacrylates.

There is a need in the industry to find an adhesive composition which exhibits pressure-sensitive adhesive characteristics useful during assembly and

which may then be converted by subsequent treatment to a structural adhesive. It is preferred that the subsequent treatment be by thermal means and could even be cured by electromagnetic induction if desired.

In use, such adhesive could be provided between two release layers or as a single tape with differential release, preferably using a release layer which is differentially releasable from an adhesive layer bonded to a backing which may also be a release surface. The adhesive could then be conveniently applied between the surfaces to be bonded. Sufficiently firm contact or light pressure established between the surfaces will cause sufficient adhesion to temporarily hold the assembly. Thereafter, heat is applied to the composite structure to convert the intermediate adhesive layer into a structural adhesive bond.

Applications for such tapes include "hem-flange" bonding and weld reinforcement in automotive, reinforcing materials for strengthening thin sheet metal and plastics by forming integral structures with the original substrate, and bonding of plastics, precoated metals, SMC, and other advanced materials.

Several attempts were made in the past to come up with a pressure-sensitive adhesive which changes into a structural adhesive after heat activation.

U.S. Patent 3,326,741 (1967) to Olson discloses a tacky pressure-sensitive adhesive which on heat activation achieves a strong permanent bond. The patent discloses a nitrile rubber/epoxy resin blend with curing agent such as dicyandiamide. However, the films did not show good cohesive strength at room temperature which is typically required for a pressure-sensitive adhesive.

U.S. Patent 3,639,500 (1972) to Muny and assigned to Avery Dennison Corporation discloses a curable pressure-sensitive adhesive composition containing a

polyepoxide, a carboxylated diene polymer, and an acrylic ester tackifier which on heat activation provides a structural bond.

U.S. Patent 4,404,246 (1983) to Charbonneau et. al discloses an alkoxylated amino formaldehyde condensate in an acrylic pressure-sensitive adhesive composition as a latent crosslinking agent to improve the cohesive strength after heat activation. However, the material behaves as a highly crosslinked pressure-sensitive adhesive after heat activation and cannot be used for structural bonding.

U.S. Patent 4,452,955 to Boeder discloses an adhesive composition consisting of a polymer dissolved in polymerizable monomer, an accelerator such as organic sulfimides and perfluoroalkylsulfonanilides, and an inhibitor. The adhesive shows pressure-sensitive adhesive properties, and after heat activation, the adhesive demonstrates properties similar to a structural adhesive. However, the properties as detailed in the examples do not show properties of true structural type adhesives, especially in lap shears.

U.S. Patent 4,404,345 (1983) to Janssen also discloses a similar adhesive composition consisting of an adhesive base as the first part and an initiator portion as the second part. Bonding methods are also described. None of the prior art described above teaches or suggests a pressure-sensitive adhesive that can be heat cured to form the strong and permanent bond of a structural adhesive.

Summary of the Invention

This invention provides an adhesive that has the ease of application of a pressure-sensitive adhesive, yet upon cure by application of heat, forms the strong and permanent bond of a structural adhesive. This adhesive is made up of a core layer of a curable permanent structural adhesive having opposed surfaces

with a thin skin of a pressure-sensitive adhesive on one or both surfaces. The core layer is preferably made up of either a partially cured B stage structural adhesive or a blend of curable polymeric material such as an epoxy with an acrylate resin and hardener which upon cure will form a structural adhesive. It is this core layer that forms the strong and permanent bond after final cure. The preferred embodiment also includes an impact improving elastomer to make the bond more impact resistant. In the most preferred embodiment, an impact absorbing agent is included in the core layer.

The skin of pressure-sensitive adhesive that is applied to one or both opposing surfaces of the core layer is inherently tacky and provides a temporary bond between the adhesive and a substrate at room temperature. This temporary bond created by the pressure-sensitive adhesive provides a means for holding two substrates together during the cure of the core layer structural adhesive. The core layer structural adhesive is cured by heating the entire assembly made up of the two substrates and the adhesive. Once the heat-cure process has been completed, a strong and permanent bond results. During cure, the skin or skins of pressure-sensitive adhesive are absorbed, presumably blending into the core layer structural adhesive.

Such an adhesive is useful in that it eliminates the need to clamp or otherwise hold substrates to be bonded together during heat cure. The skin or skins of pressure-sensitive adhesive act in place of clamps by providing a temporary bond that lasts long enough to enable the structural adhesive to be cured.

Brief Description of the Drawings

FIG. 1 is a cross section of one embodiment of the invention.

FIG. 2 is a cross section of a second embodiment of the invention.

FIG. 3 is a cross section of a third embodiment of the invention.

Detailed Description

This invention provides a novel pressure-sensitive adhesive construction which is normally tacky and forms a pressure-sensitive adhesive bond at room temperature and which on heat activation is supplanted by a structural adhesive bond. This is achieved by distributing on one or both sides of a core layer of structural adhesive a thin skin of a pressure-sensitive adhesive. If the pressure-sensitive adhesive is applied to only one side of the core layer, the other side of the core layer can be prebonded to a backing or face stock. The skin or skins of pressure-sensitive adhesive can be either continuous or discontinuous layers. Various different pressure-sensitive adhesives can be used for the skin layer or layers. For example, either acrylic- or rubber-based pressure-sensitive adhesive may be used. Additionally, the pressure-sensitive adhesive can be either one that is inherently tacky or one that requires addition of a tackifier prior to bonding. The core layer is made up of various different structural adhesives such as a partially cured B stage structural adhesive or a blend of epoxy with an acrylate ester resin and hardener. While the skin or skins of pressure-sensitive adhesive provide the initial tack, these layers are absorbed into the core layer by heat activation. This unique feature provides a pressure-sensitive adhesive with structural adhesive properties after heat activation.

Referring to the figures, three different embodiments of the invention are illustrated in FIGS. 1-3. In FIG. 1, a cross section of the adhesive is shown in which a core layer of structural adhesive is sandwiched between two continuous skin layers of pressure-sensitive adhesive 12 and 14. The illustration also shows a suitable release liner 16 which protects the pressure-sensitive adhesive and

prevents the adhesive from inadvertent bonding prior to use.

FIG. 2 is a cross section of a second embodiment of the invention in which the core layer of structural adhesive 18 is sandwiched between two discontinuous skin layers of pressure-sensitive adhesive 20 and 22. These discontinuous skin layers can take the form of stripes, dots or various other patterns of pressure-sensitive adhesive. The release liner is illustrated as 24.

FIG. 3 is a cross section of a third embodiment of the invention. In this embodiment, the core layer of structural adhesive 26 is prebonded to substrate 28. A skin layer of pressure-sensitive adhesive 30 is found on the opposite side of the core layer. Release liner 32 protects the adhesive and prevents inadvertent bonding prior to use.

This invention is useful for various applications where a strong bond between two substrates or between a backing and a substrate is desirable but difficult to achieve because the substrates are difficult to hold together while the adhesive cures. Applications for such adhesives are numerous. In the automobile manufacturing industry, such adhesives would be useful for "hem-flange" bonding and weld reinforcement by providing a temporary bond which would become permanent during the paint-bake step in manufacturing. The adhesive would also be useful in the aerospace and other industries by providing a means of easily forming integral bonds between plastics, metals and various advanced materials.

The core layer can be comprised of an epoxy resin, a polymer resin and a hardener. Typical examples of epoxy resins include Epon 828, Epon 826, Epon 836 and the like available from Shell Chemical Co., and are characterized by the presence of epoxide functionality. The resins at room temperature could be a liquid of low

molecular weight or solid resins which are higher in molecular weight. Blends of several epoxy resins of different structures, molecular weight and epoxy functionality could be used to achieve the desired balance of properties for the core layer.

The polymer resin is preferably an acrylic ester resin like polymethyl methacrylate (PMMA) and PMMA copolymers and the like. For example Acryloid Resin A 21, B 667 etc. manufactured by Rohm and Haas can be used for this application. The acrylic ester resins could be based on methyl methacrylate, butyl acrylate, and isobutyl methacrylate and the like. Other polymers or polymer blends can also be used.

Typical examples of hardeners include boron trifluoride or trichloride amine complexes like BF_3: monoethyl amine, blocked amines like HT 9506 (produced by Ciba Geigy), or Dicyandiamide (Dicy) and the like. Mixtures of a blend of hardeners could also be used. Other types of epoxy hardeners could also be used if they provide the desired stability and efficient cure during the heat activation. The hardeners would preferably be incompatible with the resin or inactive at room temperature but if compatible, the hardeners could also be encapsulated in a heat or pressure-sensitive polymer shell.

The core layer can also be comprised of a partially cured B stage epoxy resin. A typical example of such a resin is the FM-73 type manufactured by American Cyanamide. Additional fillers, modifying additives, fibers, and the like could be added to the core layer to improve the strength or modify the properties of the core layer. Due to brittleness of resins without fillers, the preferred embodiment includes fillers. Low density additives like microballoons could be incorporated if desired. Electromagnetic materials, particulate magnetizable iron, cobalt, nickel, alloys of nickel and iron, alloys

of nickel and chromium, inorganic oxides of iron, inorganic oxides of nickel and the like could be included to make the adhesive induction curable. The material could also be formulated for UHF, radio frequency, or microwave curing if desired.

The skin layer or layers of pressure-sensitive adhesive can be comprised of an acrylic pressure-sensitive adhesive such as Polytex 7000 which is produced by Avery Chemical, Division of Avery Dennison Corporation. This is a high performance pressure-sensitive adhesive within the scope of the claims of U.S. Patent 4,812,541 to Mallya et al., incorporated herein by reference. This high performance pressure-sensitive adhesive provides unusually high adhesion to high energy surfaces such as aluminum and stainless steel due to synergistic combination of a glycidyl monomer and an N-vinyl lactam monomer.

The skin layer or layers of pressure-sensitive adhesive can also be comprised of an elastomeric pressure-sensitive adhesive. Curable elastomeric pressure-sensitive adhesives are disclosed in U.S. Patent 4,948,825 to Sasaki, incorporated herein by reference. These curable elastomeric pressure-sensitive adhesives incorporate organic additives to reduce the energy requirements of a pressure-sensitive adhesive that is cured by actinic radiation.

Various other pressure-sensitive adhesives with different properties can be used for the skin layer as well. A permanent pressure-sensitive adhesive can be used, or if repositioning of the substrates to be bonded is desired prior to final cure, a removable pressure-sensitive adhesive can be used. A repositionable pressure-sensitive adhesive is disclosed in U.S. Patent Application Serial No. 741,556 to Mallya et al., incorporated herein by reference. This application discloses a repositionable pressure-

sensitive adhesive that has adhesive characteristics that vary depending on the application pressure. Furthermore, an inherently tacky pressure-sensitive adhesive can be used, or one that requires the addition of a tackifier prior to bonding.

The impact resistance of the pressure-sensitive structural adhesives disclosed in this specification tends to be low. Impact resistance can be improved by the addition of fillers, modifying additives, fibers or the like. These additives are included in the core layer at levels which provide satisfactory impact resistance and reduced brittleness. Since the skin layer of pressure-sensitive adhesive is absorbed into the core layer during cure, the impact modifier can also be added to the pressure-sensitive adhesive as well as the core layer with equivalent results.

While numerous options are available for the skin layers of pressure-sensitive adhesive that make up this pressure-sensitive structural adhesive, the preferred embodiment uses an acrylic pressure-sensitive adhesive that includes a compatible impact-improving elastomer.

Various release layers are available which may be applied to the adhesive and are useful in protecting the skin layer or layers of pressure-sensitive adhesive from inadvertently bonding prior to use. Suitable release layers are described in some detail in Chapter 23 of the <u>Handbook of Pressure Sensitive Adhesive Technology</u>, 2d Ed., edited by Donatas Satus, and incorporated herein by reference. If skin layers of pressure-sensitive adhesive are used on both sides of the core layer of structural adhesive, then release layers can be applied to both sides of the adhesive. These two release layers would preferably be differentially releasable from the adhesive layer to provide additional convenience in application.

Following are examples which more specifically illustrate the invention. In these examples, the 180°

peel adhesion is measured as described in PSTC-1, using 2 mil Mylar as face material and stainless steel substrate. The shear adhesion failure temperature (SAFT) is measured by applying the adhesive to a 2 mil aluminum strip and bonding it to stainless steel with a 2.54 cm^2 overlap. A 1.0 kg load is attached on one end and the temperature is raised at 0.5°C per minute until the adhesive fails in shear. The temperature at which the adhesive fails is regarded as the SAFT temperature.

Lap shear is determined by applying the adhesive film to a 0.64 to 1.01 mm thick by 2.54 cm strip of steel that is subsequently bonded to a second strip of steel with the same dimensions. A 1.27 cm overlap is maintained between the steel strips for a total bond area of 1.27 cm by 2.54 cm. A 0.5 mm bond thickness for the structural adhesive is maintained by using 0.5 mm spacer bars placed between the steel strips. An external force is applied to pull the strips apart, and the lap shear is measured as the force at which the bond breaks divided by the bond area. Lap shear is reported in pressure units as psi or MPa. Since the bonded steel strips are offset in nature, the measured bond failure is not purely due to shear stress, but includes cleavage and peel stresses as well. This determination of lap shear follows general engineering standards of the automobile industry.

Example 1:

A core layer was prepared by mixing 48 parts of Acryloid B66T (51% in Toluene), 16 part of Epon 828 and 8 parts of HT9506. The mixture was coated onto a Teflon FEP film to give a coat weight of 75 g/m^2. This was first dried for 15-20 minutes at room temperature and then at 70°C for 15 minutes.

A skin layer of an acrylic pressure-sensitive adhesive was prepared by solvent coating 15 g/m^2 of Polytex 7000 onto a Teflon FEP film and drying at 70°C for 15 minutes. The skin layer was then laminated on both sides of the core layer to prepare a sandwich construction.

This film gave a 180° peel adhesion of 526 N/m, shear adhesion of 441 minutes, shear adhesion failure temperature of 140°F and lap shear of 189 psi (1.3 MPa). After baking this film at 200°C for 30 minutes, it gave a lap shear of 1000 psi+ (6.89 MPa).

Example 2:

A "B" stage epoxy resin (FM-73) from American Cyanamide was used as the middle core layer.

A skin layer of pressure-sensitive adhesive (Polytex 7000) was laminated to each side of the core layer at 15 g/m^2 coat weight.

This film gave a lap shear of 37 psi. After baking at 200°C, this film gave a lap shear of 1000 + psi.

Example 3:

A core layer was prepared by mixing 66 parts of Acryloid B21 (30% in Toluene), 39 parts of Epon 828 and 12 parts of HT9506. The mixture was coated onto a Teflon FEP film to give a coat weight of 75 g/m^2. This was first dried for 15-20 minutes at room temperature and then at 70°C for 15 minutes.

A skin layer of an acrylic pressure-sensitive adhesive was prepared by coating 15 g/m^2 of Polytex 7000 onto a Teflon FEP film and drying at 70°C for 15 minutes. The skin layer was then laminated on both sides of the core layer to prepare a sandwich construction.

This film gave a 180° peel adhesion of 526 N/m, shear adhesion of 2000 minutes+, shear adhesion failure temperature of 183°F and lap shear of 174 psi (1.23 MPa). After baking at 200°C for 30 minutes, this film gave a lap shear of 1000 psi+ (6.89 MPa) typical of a structural adhesive.

Example 4:

A middle core layer was prepared by blending 227 parts of Araldite GY 6010, an unmodified liquid epoxy resin (manufactured by CIBA GEIGY), and 95 parts of Acryloid B66, in a Brabender Plasticorder using the roller mixer at 140° C until the mixture was homogenous. The temperature of the mix was reduced to 45-50°C by cooling and 32 parts of Dicyanex 200-X, a solid curing agent, (manufactured by American Cyanamide) was mixed into this mixture. This blend was then extruded as a sheet, 3 to 6 mil in thickness using the Brabender extruder. The die temperature was maintained at about 50 to 60°C. Two thin (15 g/m^2) acrylic pressure-sensitive adhesive layers were laminated on either side of this core.

This film laminated to 2 mil Mylar showed a peel adhesion of 1400 N/m on stainless steel substrate, room temperature shear of 255 minutes and SAFT of 45°C. The sample showed a lap shear of 105 psi (0.72 MPa). The lap shear of the sample after baking at 200°C for 30 minutes increased to 2800 psi (19.29 MPa).

Example 5:

A core layer was prepared by blending 300 parts of Acryloid A-21, a solid acrylic copolymer resin, heated to 175°C with 400 parts of Araldite GY-6010, an unmodified liquid epoxy resin, until homogenous, raising the temperature to 215°C and adding 44 parts of glass fiber (965-57) and mixing for about 30 minutes. The mixture was cooled to 90°C and 50 parts Hycar 1300 x 13, an acrylic copolymer, were added then the blend was mixed for an additional 30 minutes. Finally 70 parts of Dicyanex 200-X, a solid curing agent, were added and mixed for another 30 minutes. The mixture was coated onto a Teflon FEP film to give a coat weight of 550 g/m^2.

Two skin layers of Polytex 7000 adhesive film were laminated to either side of the core layer to give a coat weight of 17 g/m^2. This sample gave a 180° peel adhesion of 1020 N/m. The lap shear after baking at 196°C for 30 minutes was 1970 psi.

Example 6:

A core layer was prepared as in Example 5 to a coat weight of 625 g/m^2. Skin layers of I-406 were

laminated to either side of the core layer to give a coat weight of 10.6 g/m^2.

The film gave a 180° peel adhesion of 875 N/m. After baking at 196°C for 30 minutes, the sample gave a lap shear of 1400 psi.

WHAT IS CLAIMED IS:

1. A pressure-sensitive structural adhesive comprising a core layer of a curable structural adhesive providing opposed surfaces and having on at least one surface thereof a separate continuous or discontinuous layer of a tacky pressure-sensitive adhesive, the pressure-sensitive adhesive providing an initial adhesion between a substrate to be bonded by the cured structural adhesive, said pressure-sensitive adhesive layer being absorbed by the core layer of curable structural adhesive when a permanent thermoset bond to such substrate is formed by thermal cure of the curable structural adhesive.

2. The pressure-sensitive structural adhesive as claimed in claim 1 in which there is present an impact improving resin which is compatible with the structural adhesive and included in the core layer, the pressure-sensitive adhesive layer or the core layer and pressure-sensitive adhesive layer.

3. The pressure-sensitive structural adhesive as claimed in claim 2 in which the compatible impact improving resin is an elastomer.

4. The pressure-sensitive structural adhesive as claimed in any of claims 1 to 3 in which the core layer is comprised of partially cured B-stage epoxy resin.

5. The pressure-sensitive structural adhesive as claimed in any of claims 1 to 4 in which the core layer of curable structural adhesive is comprised of a blend of an epoxy resin with acrylate resin and hardener.

6. The pressure-sensitive structural adhesive as claimed in any of claims 1 to 5 in which the pressure-sensitive structural adhesive is on both surfaces of the core layer and the pressure-sensitive adhesive layers bond two substrates together until the core layer of curable structural adhesive is cured by application of heat.

7. The pressure-sensitive structural adhesive as claimed in any one of claims 1 to 6 in which electromagnetic materials are blended into the core layer of curable structural adhesive and the structural adhesive is themally cured by electromagnetic induction heating.

Fig. 1

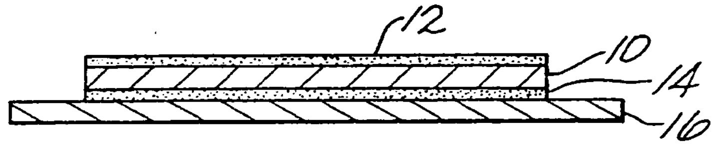


Fig. 2

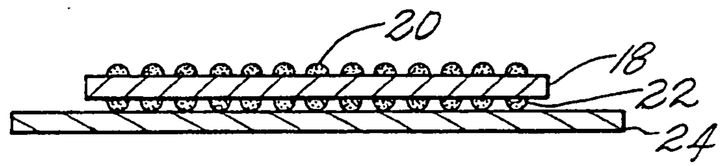
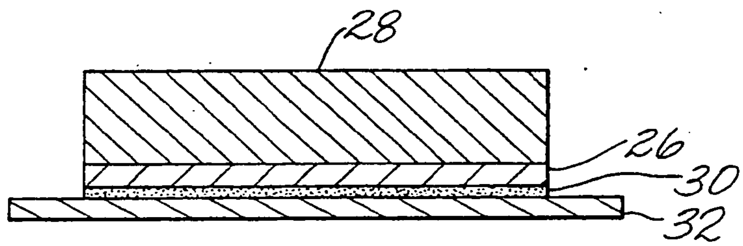


Fig. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09996

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 7/10
US CL :428/200, 343, 344, 346, 347, 354, 355
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/200, 343, 344, 346, 347, 354, 355

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,639,500 (MUNY) 01 FEBRUARY 1972. See entire document.	1-4
Y	US, A, 3,326,741 (OLSON) 20 JUNE 1967. See entire document.	1-4
Y	US, A, 4,948,825 (SASAKI) 14 AUGUST 1990. See column 2, lines 25-36.	2-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 01 December 1993	Date of mailing of the international search report JAN 03 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer CHRISTOPHER BROWN
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/09996

Box I Observations wher certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-7
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.